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Title: BAND STRUCTURE AND ELECTRICAL PROPERTIES OF AMORPHOUS SEMICONDUCTORS

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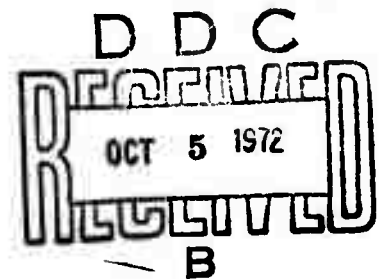
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SUMMARY OF RESEARCH

1.0 ELECTRICAL AND OPTICAL PROPERTIES OF AMORPHOUS SEMICONDUCTORS

1.1 Electrical Conductivity in Disordered Systems

Personnel: David Adler, Laurence P. Flora, Stephen D. Senturia

The semiclassical theory of electrical conductivity of disordered systems has been investigated using a Monte Carlo technique. Both analog and digital solutions of the two- and three-dimensional conductivity of a heterogeneous lattice have been obtained and found to be in agreement. As opposed to the percolation probability, which indicates sharp behavior, the electrical conductivity exhibits only a gradual rise with the fraction of conducting sites. For the three-dimensional problem, the bulk conductivity obeys the relation,

$$\sigma(p) = A(p - p_c)^2 ,$$

where p is the fraction of conducting sites, p_c is the critical value for percolation (0.30 for a simple cubic lattice), and A is a constant. If the disorder is Gaussian, as is the case for many systems of physical interest, the temperature dependence of the electrical conductivity can be evaluated. For relatively symmetric valence and conduction bands and band tails of the order of tenths of an electron volt, plots of the logarithm of the calculated conductivity as a function of $T^{-1/4}$ were essentially linear from 77K through 300K, in agreement with a great deal of experimental data. In this case, however, such behavior does not indicate the predominance of hopping in the vicinity of the Fermi energy, but rather band-like conduction in the absence of a sharp mobility edge.

1.2 Crystalline and Amorphous Silicon Telluride

Personnel: David Adler, Kurt E. Petersen

Thin-film and bulk samples of silicon telluride glasses, $\text{Si}_x\text{Te}_{1-x}$, with $0.02 \leq x \leq 0.25$, have been prepared and examined by optical absorption, photoconductivity, infrared transmission, electrical conductivity, DTA, EPR, and x-ray measurements. The resistivity, energy gap, and glass transition temperature all increase with increasing silicon concentration. No EPR signal could be detected in the bulk glasses down to 4K. The results on the glasses have been compared to similar measurements previously reported on Si_2Te_3 crystals. Even though the bonding shifts from primarily ionic in the crystal to primarily covalent in the glasses, the short-range order and infrared absorption bands are essentially the same in the amorphous and crystalline systems. The random covalent structural model is consistent with all the data obtained on the silicon telluride glasses.

1.3 Transport Studies of As_2Se_3 - Sb_2Se_3 Glasses

Personnel: David Adler, Virgil G. Cox

Electrical conductivity and thermoelectric power have been measured on several glasses in the pseudo-binary $(\text{As}_2\text{Se}_3)_{1-x}(\text{Sb}_2\text{Se}_3)_x$ system over the temperature range 300-470K. The activation energies obtained from both conductivity and thermopower are equal within experimental accuracy for $0.0 \leq x \leq 0.2$. For larger values of x , the activation energies also appear to be the same, although the possibility of partial devitrification during the experiment precludes a more definitive conclusion at this time. The thermoelectric power was found to be p-type for all samples investigated. The activation energy drops essentially linearly from 0.94 eV for $x = 0.0$ to 0.76 eV for $x = 0.4$.

2.0 SWITCHING IN CHALCOGENIDE GLASS FILMS

2.1 Experimental Studies of Threshold Switching

Personnel: David Adler, Floyd O. Arntz, Bimal P. Mathur, Donnie K. Reinhard

A comprehensive study of threshold switching in 1μ sputtered films of a chalcogenide glass of composition $\text{Te}_{40}\text{As}_{35}\text{Se}_{15}\text{Ge}_7\text{P}_3$ has been carried out. The switching time is too fast to measure; however, the delay time ranges from several microseconds to several nanoseconds, depending on the input power. The observed lifetimes are strongly dependent on the circuit used. Small load resistors, corresponding to large device currents, and large parasitic capacitances, resulting in large charging and discharging currents, reduce the lifetime considerably. The longest lifetimes are observed when the applied voltage pulse is only slightly longer than the delay time, so that the device is in the ON-state for a short time. The devices fail when they cannot be returned to the OFF-state, although often failed devices can be resuscitated by a short, intense current pulse, just as if it were a memory switch. This is strong evidence that failure is associated with devitrification of the conducting filament. The probability of devitrification is reduced by limiting the device current. Threshold devices were fabricated which routinely survived $10^7 - 10^9$ switching cycles.

If devices are switched on a pulse train, the delay time is much longer on the first pulse than on succeeding pulses, even if the polarity is reversed between pulses. To return to the virgin state, a recovery time of the order of several minutes is necessary. Alternatively, if the device is rapidly switched at frequencies greater than the order of one kilohertz, the delay time stabilizes at a new steady state with a greatly reduced value.

The pre-switching behavior is non-ohmic, with an exponential increase in current with increasing voltage always observed just below threshold. The photoconductivity results indicate that this increase in conductivity is a carrier-concentration rather than a mobility effect. This is most likely a manifestation of the Poole-Frenkel effect. At lower voltages, the current increases as $\exp(V^{1/2})$, indicative of Schottky emission from the electrodes.

2.2 Optical Absorption and Photoconductivity Measurements on Chalcogenide-Glass Films

Personnel: David Adler, Floyd O. Arntz, Donnie K. Reinhard

A comprehensive study of optical and photoconductive properties of a sputtered chalcogenide film of composition $\text{Te}_{40}\text{As}_{35}\text{Ge}_7\text{Si}_{15}\text{P}_3$ has been completed. Optical absorption results yield a linear dependence of $(\alpha h\nu)^{1/2}$ on photon energy, indicating a room-temperature optical gap of 1.1 eV. The quantum efficiency of the photoconductivity appeared to be unity. However, the relative photocurrent decreased with increasing applied electric field. Four major conclusions follow from the photoconductivity results: (1) Threshold switching is not significantly enhanced by a photon flux of 5×10^{15} photons/cm²-sec; (2) the exponential increase of dark conductivity with electric-field intensity is primarily a carrier-concentration rather than a mobility effect; (3) depletion layers exist at molybdenum-chalcogenide junctions; (4) hole conduction in these chalcogenides dominates electron conduction. From the polarity of the zero-bias photocurrent, it can be concluded that the chalcogenide bands bend up at the interface with molybdenum electrodes.

2.3 Electron-Bombardment-Induced Conductivity in Chalcogenide Films

Personnel: Floyd O. Arntz, Donnie K. Reinhard

EBIC currents resulting from bombardment by 5-20 KeV electrons have been studied as a function of applied voltage on 1μ chalcogenide films. A threshold energy of 8 KeV for the appearance of the EBIC signal indicates a schubweg (mean trapping distance) of much less than 1μ . The observed EBIC gain is quite low, and the calculated free carrier lifetime is of the order of 10^{-12} sec. This low lifetime is consistent with small mean free paths. The bias dependence of the signal decay time provides strong evidence for a junction capacitance between the molybdenum electrode and the chalcogenide film.

2.4 Chalcogenide Glass-Silicon Heterojunctions

Personnel: Floyd O. Arntz, Donnie K. Reinhard

Chalcogenide glass-silicon heterojunctions have been fabricated by rf sputtering the chalcogenide directly onto a polished, chemically cleaned silicon wafer. Results for p-type Si heterojunctions indicate a saturation current when the chalcogenide is positively biased, while the reverse polarity produces a rapid increase in current once the magnitude of the bias exceeds two volts. For voltages below two volts, the junction is blocking for both polarities. For n-type Si heterojunctions, no saturation current is observed for either polarity, and the forward current does not increase as rapidly as does the p-type heterojunctions. Nevertheless, the characteristics can be described as rectifying in both cases.

Photoconductivity of these heterojunctions also has been investigated. For the p-type heterojunctions, the reverse saturation current increases with increasing light intensity, yielding photo-diode behavior. A white-light in-

tensity of 10 mw/cm^2 is sufficient to increase the reverse current by a factor of 40. The forward current is only slightly affected by the incident photons. With the n-type heterojunctions, both the forward and reverse currents are increased by the incident light. In the reverse direction, the saturation portion of the I-V characteristic is increased, similar to the p-type results. With a positive bias, the forward current is increased by photon bombardment, resulting in a forward characteristic similar to the high-conductivity portion of the reverse characteristic.

At sufficiently high fields, both the p-type and n-type heterojunctions exhibit switching behavior. However, the threshold voltages and threshold currents depend on both polarity and silicon doping. For reverse biases, switching occurs only after avalanche breakdown in the silicon. In the n-type heterojunctions with forward bias, switching can be induced by incident photons.

All of these experimental results can be explained by a simple band model in which the chalcogenide bands bend up and the silicon bands bend down for p-type heterojunctions, while the bands remain flat for n-type heterojunctions. An analysis of the switching nature of the heterojunctions indicates that the switching is at least partially controlled by a contact phenomenon.

2.5 Four-Probe Conductivity Measurements on Chalcogenide Devices

Personnel: David Adler, Floyd O. Aantz, Bimal P. Mathur, Stephen D. Senturia

Four-probe measurements of chalcogenide-glass switching devices have been carried out, in the virgin, switching, and formed states. Although contact resistance is significant, it can be concluded that the formation

process cannot entirely be due to a reduction of the voltage across the electrode chalcogenide interfaces. At least two other effects can be shown to be important, the change in conductivity from Joule heating of the filament in the ON-state and the formation of small crystallites within the filament. Further measurements are in progress.

2.6 Low-Temperature Studies of Threshold Switching

Personnel: David Adler, Laurence P. Flora

Threshold switching in chalcogenide films has been investigated down to 4K. No qualitative differences are found in switching characteristics, even at liquid He temperature. This is in disagreement with electronic models for switching that depend on double injection through narrow Schottky barriers, since these barriers are frozen in for at least the order of months at 4K. However, turn-off and reswitching occur in the normal manner at these temperatures. The non-ohmic pre-threshold effects at low temperatures appear to follow a power law rather than an exponential in most cases. Devices that have been formed at room temperature show further formation effects at liquid helium temperature. The evidence indicates that partial devitrification of some of the material occurs during switching at low temperatures, and this appears to be the dominant effect in the formation processes.

2.7 Electrothermal Models for Threshold Switching

Personnel: David Adler, Theodore Kaplan

Electrothermal switching models have been theoretically analyzed as a mechanism for threshold switching in chalcogenide glasses. Numerical techniques have been developed for simultaneously solving the set of steady-state electric and heat current flow equations, the energy-conservation equation, and Maxwell's equations in three dimensions. Solutions of these equations

have been obtained for a material with an electrical conductivity either of the form

$$\sigma = \sigma_0 \exp (-\Delta/kT) ,$$

independent of electric field, or of the form

$$\sigma = \sigma_0 \exp (-\Delta/kT + E/E_0) ,$$

where E is the electric field intensity. In the former case, no differential negative resistance is obtained unless there is significant heating of the electrodes or Schottky emission or space-charge effects occur. The latter case always gives current-controlled differential negative resistance and high-temperature filamentary conduction paths between the electrodes. However, the solutions are strongly dependent on the electrical and thermal boundary conditions at the electrodes. As soon as the results of four-probe conductivity measurements are available on actual switching devices, the predictions of the electrothermal theory will be compared with experiment.

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1. Theodore Kaplan, "Electrothermal Mechanisms for Threshold and Memory Switching in Amorphous and Crystalline Semiconductors," Ph.D., Department of Electrical Engineering, June, 1972.
2. Virgil G. Cox, "Transport Properties of Several Amorphous Semiconductors," S.M., Department of Electrical Engineering, June, 1972.
3. Kurt E. Petersen, "Properties of Crystalline and Amorphous Silicon Telluride," S.M., Department of Electrical Engineering, June, 1972.

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16. D. Adler, "Electronic Aspects of the β - ω Phase Transition," to be published.

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